

Chapter 4

Characterization of the Low-Curing-Temperature Silver Paste with Silver 2-ethylhexanoate Addition

In this chapter, the effects of the solvent and atmosphere on the thermal decomposition behaviors of the silver 2-ethylhexanoate and α -terpineol were investigated. Low-curing-temperature silver pastes from Ag flake, α -terpineol and various amounts of silver 2-ethylhexanoate were prepared and characterized. The microstructures and resistivities of the cured films screen-printed from the pastes were examined. The results of thermal analysis (DSC, TGA, and TGA-MS) in oxidizing and reducing atmospheres reveal that thermal decomposition is the dominating reaction during heating process of silver 2-ethylhexanoate, even though the DSC result reveals exothermic reaction for silver 2-ethylhexanoate heated in air due to oxidation. After thermal decomposition, it leave almost pure Ag particle, which is beneficial to provide the bridging between silver flake particles in the films. Based on the rheological behavior, microstructural evolution and electrical evaluation, it can be concluded that the low-curing-temperature silver paste with 5wt% of silver 2-ethylhexanoate additions is the best formulation evaluated, which possesses shear-thinning and thixotropy properties and the resistivity of $7.8 \times 10^{-6} \Omega\text{-cm}$ after cured at 250°C , which is relatively close to the bulk resistivity of Ag.

4-1 Introduction

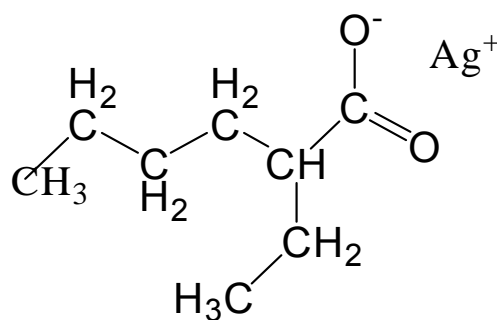
Recently, researcher has been tremendous interest in development of low-cost, disposable microelectronic devices on a flexible substrate such as radio frequency identification (RFID) tags, smart cards, and other similar items. Screen-printing, electro-photographic printing and ink-jet printing have been used to form a precise electrically-conductive pattern by depositing metal particles onto an insulating substrate surface. Especially screen-printing and ink-jet printing have been used for printing the antennas in RFID tags [1,2].

For the flexible electronics, all of the components must tend towards a low temperature processing, well adhesion in polymer-based substrates, low cost and high-speed manufacturing, and high performance. Most commercial conductive inks designed for the various printing processes are formulated using conducting metal particles as the conducting phase while resins are used as the binders and vehicles. The binder and vehicles are generally nonconductive which may hinder the metal powder contact and reduce the electron transmission.

Recently, low-curing-temperature conductor technology with metallo-organic decomposition (MOD) compound additions was investigated to form a three dimensional metal network. MOD compounds are generally synthetic metallo-organic salts that can decompose completely at low temperatures to precipitate metal or oxide, depending on the metal and atmosphere. K.F. Teng etc. [3] used ink-jet printing to lay down silver neodecanoate MOD ink on various substrates to obtain Ag film with nearly bulk conductivity. They also [4] applied the MOD inks on the metallization of solar cells. With appropriate thermal processes, it could improve the contact resistance

and the efficiency of the solar cells. Dearden and his co-workers [5] utilized the synthesized silver carboxylate (silver neodecanoate) in a nonpolar organic solvent (xylene) to form a silver ink and was applied using ink-jet printing to produce conductive tracks. The results showed that the resistivity values were dropped down to a value of few times the theoretical resistivity of bulk silver after heat-treated at the temperatures of 150°C. Parelec Inc. patented a conductor ink with the addition of the MODs [6,7]. Two kinds of MOD compounds, including silver neodecanoate and silver 2-ethylhexanoate, were used. They were mixing with silver flake powder and α -terpineol to form a silver paste. The MOD-metal flake mixture maintains its configuration during heating, and decomposes to form a well-bonded, well-resolved conductor at a temperature of approximately 200°C and deposit to a temperature above about 300°C. The electrical conductivity of the resultant film is comparable to that obtained by conventional thick film fired at high-temperatures.

Previous study [10] indicated that 2-ethylhexanoate ($C_8H_{15}O_2Ag$) possesses a very low decomposition temperature (190.3°C) among the MOD agents, and it forms silver particles to promote the linking among silver flake particles and thus reduces the resistivity to $<13 \mu\Omega\text{-cm}$ at a temperature as low as 200°C. The silver 2-ethylhexanoate was the derivatives compound from silver neodecanoate, and its molecule structure was showed as below.



Silver 2-ethylhexanoate

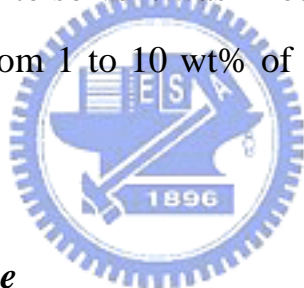
In this chapter, the low-curing-temperature silver pastes with additions of various amounts of silver 2-ethylhexanoate were prepared. The effects of the solvent and atmosphere on the thermal decomposition properties of the vehicle were characterized through the thermogravimetry analyzer (TGA), differential scanning calorimeter (DSC) and thermogravimetry analyzer mass spectrographic (TGA-MS). The rheology behaviors for the various pastes were investigated. The pastes were screen-printed on alumina substrate as spiral lines and then thermally treated at a range of temperatures. The microstructures and resistivities of the resulted films were characterized and discussed. The roles of silver 2-ethylhexanoate in the low-curing-temperature silver paste were discussed.



4-2 Experiment Procedure

4-2-1 Paste Preparation

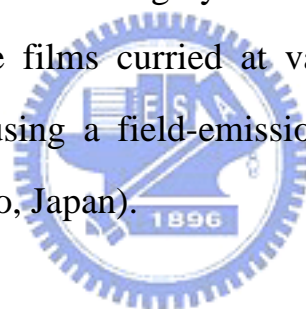
The low-curing-temperature silver pastes used in this study were prepared from Ag flake (Ferro, U.S.A.), metallo-organic compound of silver 2-ethylhexanoate, and solvent of α -terpineol. All materials were mixed by a high-speed mixer (Thinky Mixer) for 3 min and De-bubble for 1min. Subsequently, uniform pastes were formed using a triple-roller grinder (EXERT, Germany), which causes the breakdown of pigment agglomerates. The weight ratio of silver flake powder to solvent was fixed at 21:79. The additions of silver 2-ethylhexanoate varied from 1 to 10 wt% of the total silver flake powder and solvent.



4-2-2 Characteristic Analyze

In order to understand the thermal behavior of silver 2-ethylhexanoate (STREM, U.S.A.) in various solvents, including 2-ethylhexanoate acid (ACROS Organics, Belgium), α -terpenol (TCI, Japan), alcohol (J.T. Baker, U.S.A.), and n-Hexene (Schariau Chemie S.A., Spain), thermal analysis using the thermogravimetry analyzer (TGA; Perkin-Elmer) and differential scanning calorimeter (DSC; Perkin-Elmer Diamond) were performed under air and N₂ atmospheres at a heating rate of 10°C/min. The TGA traces were derivatively calculated to identify the thermal decomposition temperatures at which the mass loss is at a maximum. For the DSC experiments on silver 2-ethylhexanoate, a

sample of approximately 10mg was placed in an aluminum open pan under air and N₂ purge gas, and the heat flow was recorded. On-line TGA-MS measurements were performed simultaneously on silver 2-ethylhexanoate using the STA-409CD with Skimmer coupling (Netzsch, Germany), which is equipped with a quadrupole mass spectrometer QMA-400 (Balzer). The measurements were made at a heating rate of 10°C/min in an atmosphere of He or dry air. The attenuated total reflectance (ATR) FT-IR on the silver 2-ethylhexanoate, α-terpineol, and their mixture were performed to understand the chemical bonding among various species. The rheological measurements of the pastes were explored using a shear stress controlled rheometer (HAAKE RS150) with a plate-plate measuring system (35 mm diameter, gap 0.5 mm). The microstructure of the films curried at various temperatures and holding times were investigated using a field-emission scanning electron microscope (SEM; JEOL-6500F, Tokyo, Japan).



4-2-3 Sample Preparation and electrical measurement

Spiral silver metal lines with a length (l) of 216 cm, a line width (w) of 0.8mm and a line thickness (d) of 20~40 μ m were screen-printed on alumina substrate for the resistivity measurement. A Keithely 2400 multimeter with a four-point probe was used to measure the resistance of cured silver paste. The resistivity of the silver conducting line cured at the various temperatures was calculated using the relationship $\rho = (R \cdot w \cdot d) / l$, in which the R is the resistance of the spiral.

4-3 Results and Discussion

Figure 4-1 shows the thermal decomposition characteristic of silver 2-ethylhexanoate dissolved in various solvents, including 2-ethylhexanoate acid, alcohol, α -terpenol, and n-hexene. The results indicate that thermal decomposition of silver 2-ethylhexanoate is near 190°C. There are obvious peaks of maximum weight loss correspond to the evaporation or oxidation of 2-ethylhexanoate acid, alcohol and n-hexene at 254.5, 141.5 and 82.0°C, respectively. Solution of silver 2-ethylhexanoate in α -terpenol solution behaves differently. Only a thermal decomposition at 213.5°C is observed, which elucidates the homogeneous distribution of the chemical species. **Figure 4-2** shows the results of FT-IR for pure silver 2-ethylhexanoate, α -terpenol and their solution. Carefully examining the curves, there are no new absorption peak appeared in the IR spectrum for the mixture, which manifests that no reaction bond formed when silver 2-ethylhexanoate mixed with the α -terpenol.

The DSC curves of silver 2-ethylhexanoate in air and N₂ atmosphere are shown in **Figure 4-3**. An exothermic peak apparent appeared at 260°C with the calculated heat capacity (ΔH) of 648.91 J/g in air. However, an ambiguous exothermic peak in N₂ atmosphere, which suggests a weak oxidation occurs. The thermogravimetric analysis (TGA) and the subsequent derivative thermogravimetric analysis (DTG) of the pastes in air and N₂ atmospheres were shown in **Figure 4-4(a)** and **Figure 4-4(b)**, respectively. The TGA results reveal a weight loss of ≈ 56.9 wt% and 56.7 wt% in the temperature ranging between 150°C and 240°C for air and N₂ atmosphere, respectively. The derivative weight changes shown at DTG results have the decomposition temperatures at 231.9°C

in air and 234.7°C in N₂. TGA and DTG results shown that the total weight losses in both atmospheres are similar and the temperature of thermal decomposition occur in reduction atmosphere is a little higher than in oxidation atmosphere. After TGA experiments at temperatures above 300°C, the residues are close to the theoretical weight percentage of Ag in silver 2-ethylhexanoate (43.4 wt%) based on the chemical formula. This apparently indicates that thermal decomposition of the silver 2-ethylhexanoate can completely proceed and leave almost pure Ag, which is beneficial to provide the bridging between silver flake particles in the films.

Table 4-1 summarized the gases evolved during heat treatment of silver 2-ethylhexanoate, analyzed by means of TGA-MS in air and He atmospheres. The results shown that, in air atmosphere, the decompositions of all organic species occurred at temperatures between 180 and 350°C. In the He atmospheres, the evolutions of various species are generally similar to those observed in air. Except that the H₂O ($m/z=18$) at temperatures range 50 to 350°C, and CH₂CO, CH₃CO, and C₃H₆ ($m/z=42$) at temperatures between 180 and 350°C were observed. Also, C₄H₉ ($m/z=57$) were not appeared. The C₈H₁₅O ($m/z=127$) were evolved at lower temperatures (220 to 250°C) under oxidizing atmosphere. While the TGA and TGA-MS were performed in different gas (N₂ and He atmospheres, respectively), the results are good indication of the thermal behavior of the MOD compound in the reducing atmosphere. The TGA-MS results demonstrate that C₂H₄ is the major gas during thermal decomposition of silver 2-ethylhexanoate in oxidizing atmosphere, while C₂H₄, CH₃COOH, H₂O, and C₅H₁₀O in reducing atmosphere. Combining TGA and TGA-MS results both reveal thermal decomposition is the dominating reaction during heating process of silver 2-ethylhexanoate, even though the DSC result reveals exothermic

reaction for silver 2-ethylhexanoate heated in air due to the oxidation.

Figure 4-5 shows the viscoelastic relaxation spectrum of rheology measurement for α -terpenol with the addition of 5 wt% silver 2-ethylhexanoate at shear stress 1 Pa, which indicates the material response to impact or gradual load. The storage G' and loss G'' moduli linearly decrease with decreasing frequency, which indicates that the stress relaxation is very rapid. The $\tan\delta = G''/G'$ reveals the viscoelastic behavior of silver 2-ethylhexanoate in the α -terpenol [11]. As the $\tan\delta \gg 1$ (relaxation time $\ll 9$ sec), the mixture is non-agglomerate. The slope of G' modulus indicates the mixture containing unlinked molecules with a narrow molar mass distribution [11]. The results show the crossover point of $G' = G''$ at frequency of 9 sec., which indicates the material relaxation time and determines the onset of agglomeration for the silver 2-ethylhexanoate mixed with the α -terpenol. As the frequency larger than the relaxation time, silver 2-ethylhexanoate becomes agglomerated in the α -terpenol solvent.

The rheological viscosities of the pastes with additions of various amount of silver 2-ethylhexanoate were shown in **Figure 4-6(a)**. It shows that all pastes appear pseudoplastic flow (shear-thinning) property. The additions of 1wt%~5wt% silver 2-ethylhexanoate indicates a steady viscosity properties for increasing shear rate. Nevertheless, at higher MOD additions (>5 wt%), the paste shows shear-thinning with an apparent yield point and paste structure was destroyed in higher shear rate. The higher the silver 2-ethylhexanoate content, the higher the apparent yield point. This is consistence with the results shown in **Figure 4-5**, as the MOD addition increases, the elasticity contributed from the α -terpenol solvent decreases, which leads to the paste structure and viscoelasticity to be destroyed.

The thixotropic properties of the pastes with various amounts of silver 2-ethylhexanoate additions were shown in **Figure 4-6(b)**. The thixotropy is directly related to the silver paste operational feasibility, printability and pattern definition. The larger the hysteresis area between the curves, the slower restructuring occurs. For the silver paste with 1wt% silver 2-ethylhexanoate addition, it shows the no thixotropy properties. When increased to 3wt% and 5wt% of the silver 2-ethylhexanoate additions, the thixotropy properties were obtained with apparent clear hysteresis area. However, as the MOD compound over 5wt%, the paste lost its viscoelasticity at high shear rate.

Figure 4-7 show the resistivity of low-curing-temperature silver paste with various amounts of silver 2-ethylhexanoate additions and cured at different temperatures for 10 min. The thermal decomposition of silver 2-ethylhexanoate generates metallic silver and organic gas [8,9]. The metallic silver particles provide the bridging of the silver flake particles and thus increase the conductivity of the metal film. However, the results show that, at the lower silver 2-ethylhexanoate additions (1 wt% or 3wt%), they are not enough to form a sufficient linking between the silver flake particles and leads to high resistivities. With the addition of 5wt% silver 2-ethylhexanoate, the resistivity of the film reaches a minimum value, which are 7.8×10^{-6} , 6.8×10^{-6} and 6.4×10^{-6} Ω -cm when cured at 250, 300, 350°C, respectively, which is relatively close to the bulk resistivity of Ag (1.6×10^{-6} Ω -cm). As the MOD addition over the 5wt%, the resistivity is increased again. This is due to the facts that the high viscosity and low leveling characteristic of the pastes increase the internal holes and agglomeration of metal powder, which reduces the connectivity of silver flake particles.

Figure 4-8 shows the SEM micrographs of low-curing-temperature silver

paste with various amounts of silver 2-ethylhexanoate additions and cured at 250°C for 10min. Additions of 1wt% and 3wt% silver 2-ethylhexanoate were not sufficient to provide the linking between silver flake particles and thus microstructures with no bridging between grains were observed. The microstructure of the film with 5wt% silver 2-ethylhexanoate addition shows neckgrowth between silver particles, which confirms the low resistivity value shown in **Figure 4-7**. For the 8wt% of silver 2-ethylhexanoate addition, the resistivity of the film increases after curing due to the low bridging between the metal particles. The microstructure reveals the grains lacking neckgrowth and the existence of grain agglomeration. This is due to the facts that a non-uniformity of the silver 2-ethylhexanoate in the solvent and the viscosity of the paste is so high which results in agglomeration of silver flake particles.



4-4 Summary

The thermal decomposition is the dominating reaction during heating of silver 2-ethylhexanoate in both oxidizing and reduction atmospheres. Low-curing-temperature silver pastes from Ag flake powders, α -terpineol and various amounts of silver 2-ethylhexanoate were prepared. The paste with 5wt% of silver 2-ethylhexanoate additions is the best formulation studied, which possesses shear-thinning and thixotropy properties and the resistivity of $7.8 \times 10^{-6} \Omega\text{-cm}$ after cured at 250°C , which is relatively close to the bulk resistivity of Ag.



References:

1. D. Redinger, S. Yin, R. Farschi and V. Subramanian: IEEE. Trans. Electron. Devices. 51 (2004) No. 12, 1978.
2. V. Subramanian, Paul C. Chang, J. B. Lee, A. R. Murphy, D. R. Redinger and S. K. Volkman: Proceeding of the IEEE. 93 (2005) No. 7, 1330.
3. K. F. Teng and R. W. Vest: IEEE. Trans. Components, Hybrid, and Manufacturing. V CHMT-12 (1987) No. 4, 545.
4. K. F. Teng and R. W. Vest: IEEE. Trans. Components. Hybrid, and Manufacturing. 11 (1998) No. 3, 291.
5. A. L. Dearden, P. J. Smith, D. Y. Shin, N. Reis, B. Derby, and P. O'Brien: Macromol. Rapid Commun. 26 (2005) 315.
6. P. H. Kydd: PCT pattern WO 98/37133 (1998).
7. P. H. Kydd: U. S. Patent 6036889 (2000).
8. S. J. Lee, S. W. Han, H. J. Choi and K. Kim: J. Phys. Chem. 106 (2002) B2892.
9. N. F. Uvarov, L. P. Burleva, M. B. Mizen, D. R. Whitcomb and C. Zou: Solid State Ionics. 107 (1998) 31.
10. C.A. Lu, P. Lin, H.C. Lin and S.F. Wang: to be published in Jpn. J. Appl. Phys.
11. T.G. Mezger: in *The Rheology Handbook*, ed. U. Zoril, Vincentz Verlag (Hannover, Germany, 2002).

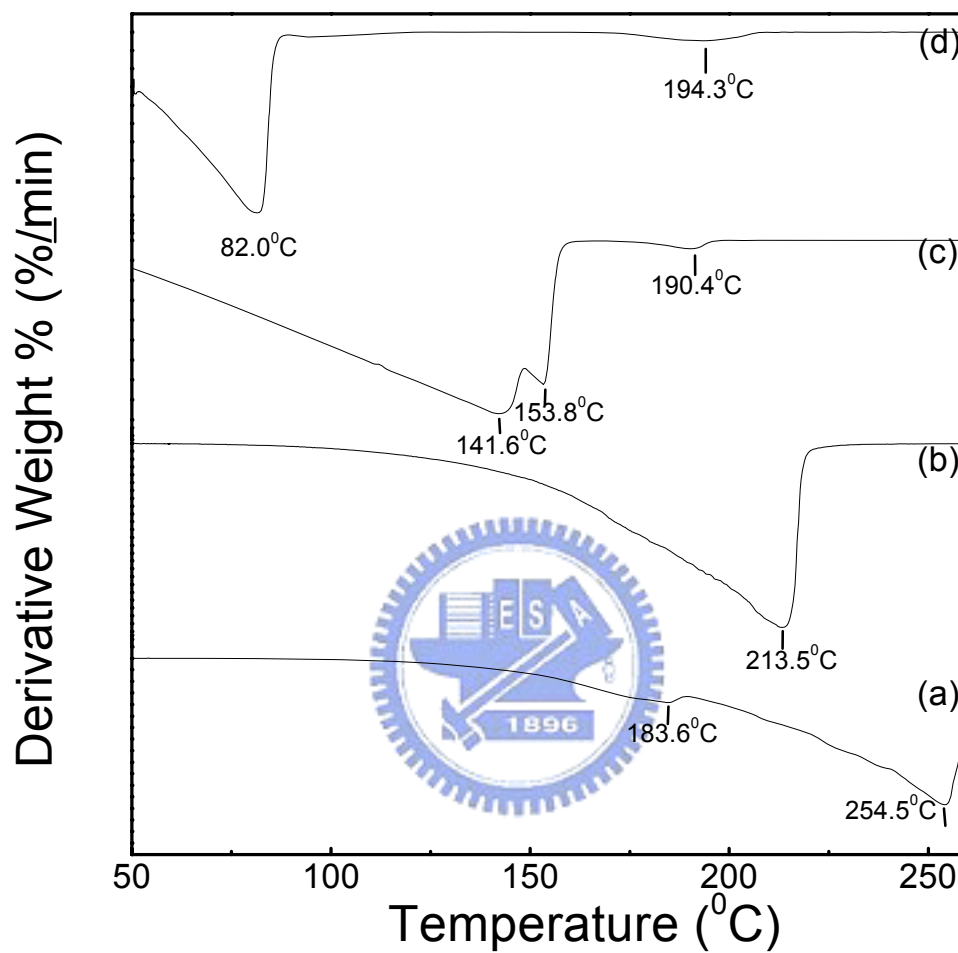


Figure 4-1. Derivative thermogravimetric analysis of silver 2-ethylhexanoate mixing with (a) 2-ethylhexanoate acid, (b) α -terpenol, (c) alcohol, and (d) n-hexene..

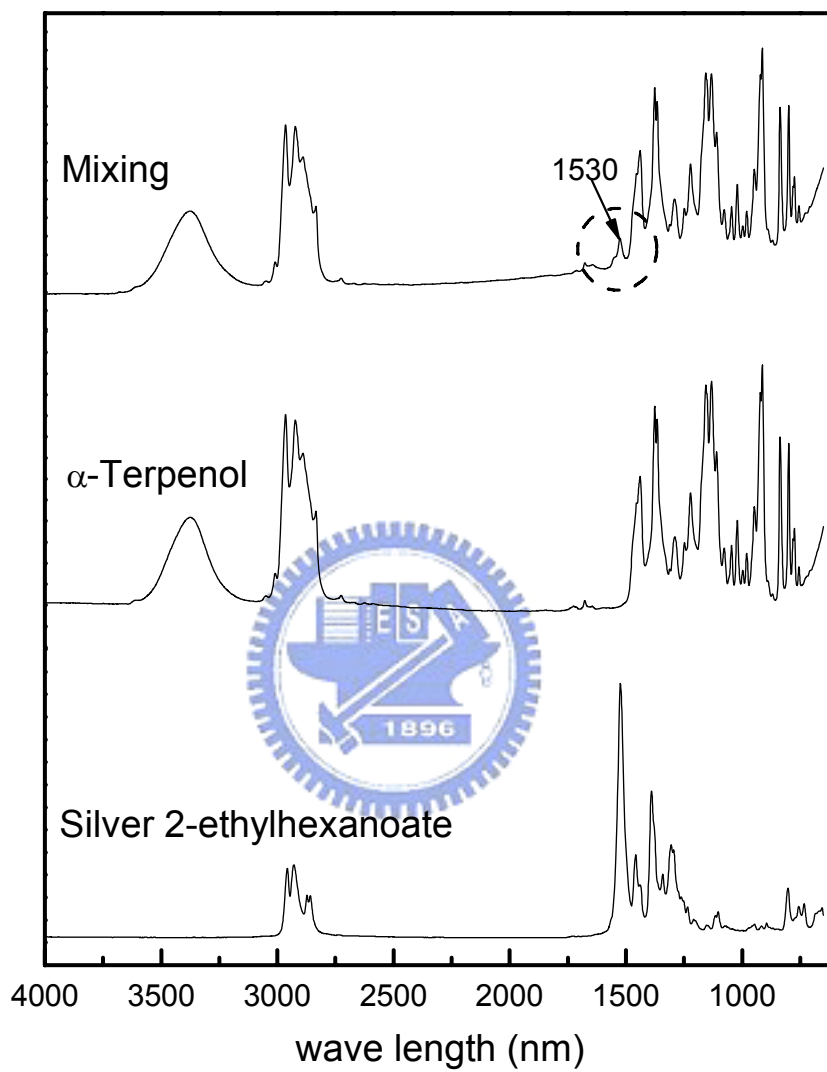


Figure 4-2. IR spectrum analysis of the pure silver 2-ethylhexanoate, pure α -terpenol and their mixture.

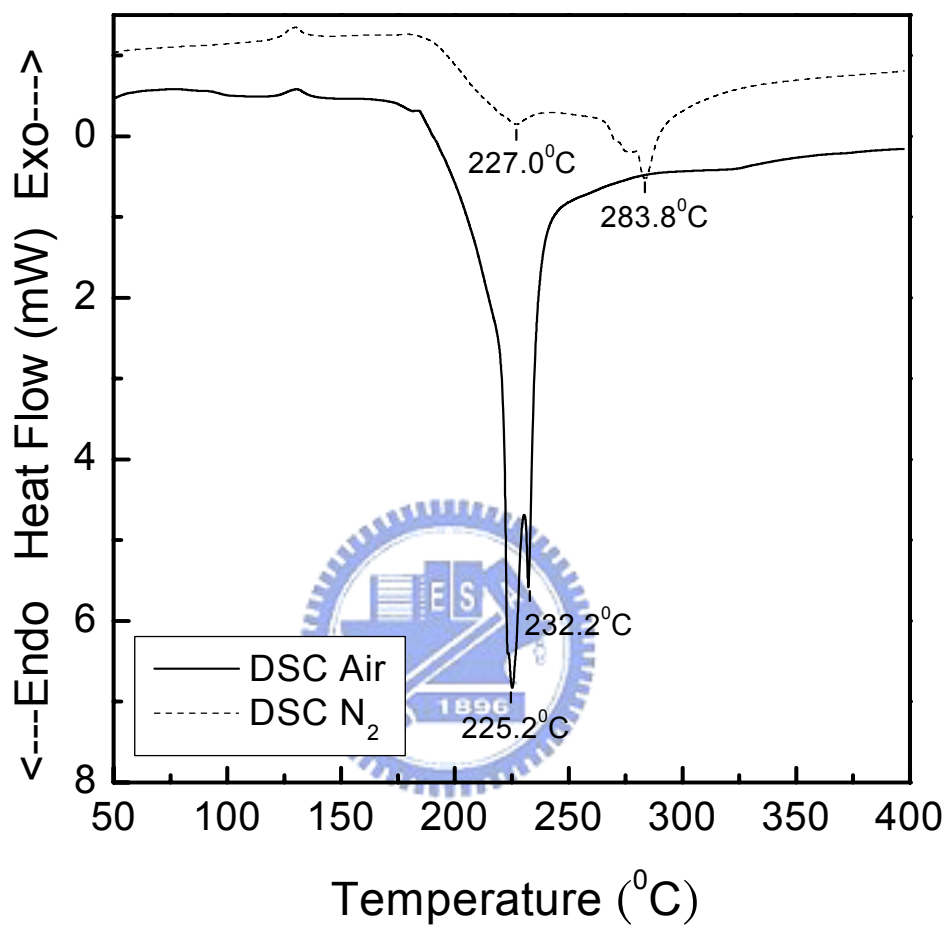


Figure 4-3. Differential scanning calorimeter analysis of the silver 2-ethylhexanoate in (a) Air, and (b) N₂.

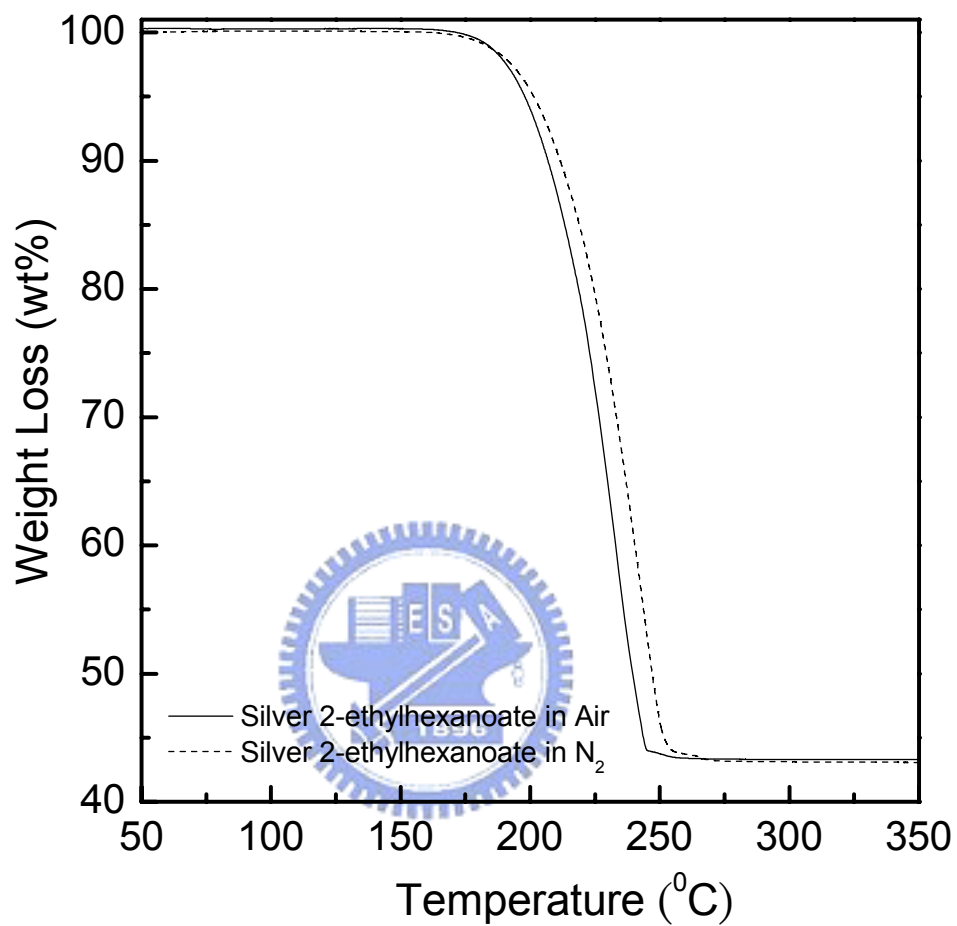


Figure 4-4(a). (a) Thermogravimetric analysis, and (b) Derivative thermogravimetric analysis of the silver 2-ethylhexanoate in air or N₂.

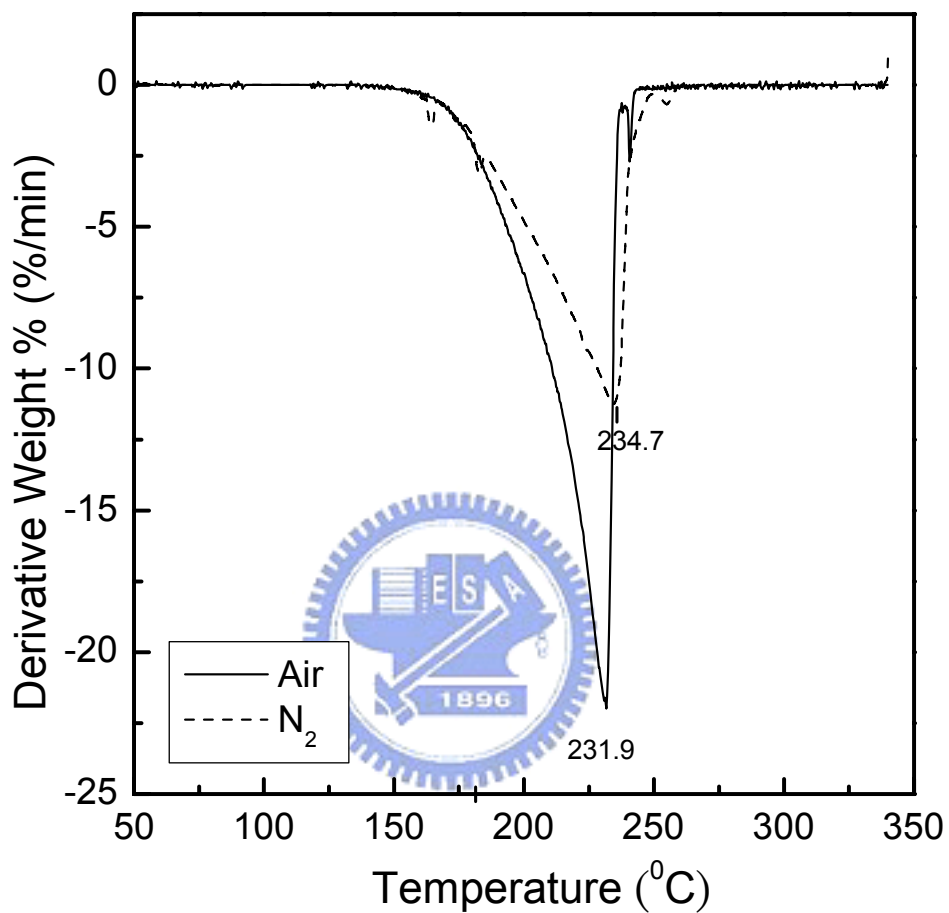


Figure 4-4(b). (a) Thermogravimetric analysis, and (b) Derivative thermogravimetric analysis of the silver 2-ethylhexanoate in air or N₂.

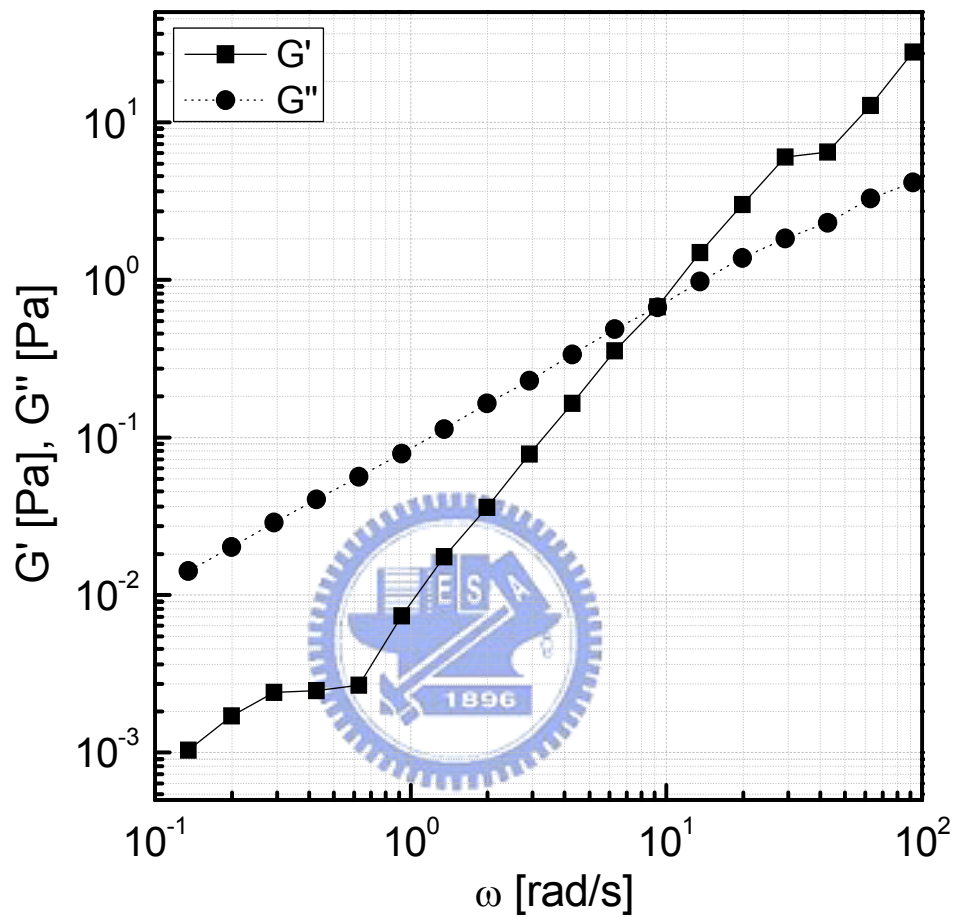


Figure 4-5. Viscoelastic relaxation spectrum of rheology measurement for α -terpenol with 5wt% of silver 2-ethylhexanoate at shear stress 1 Pa.

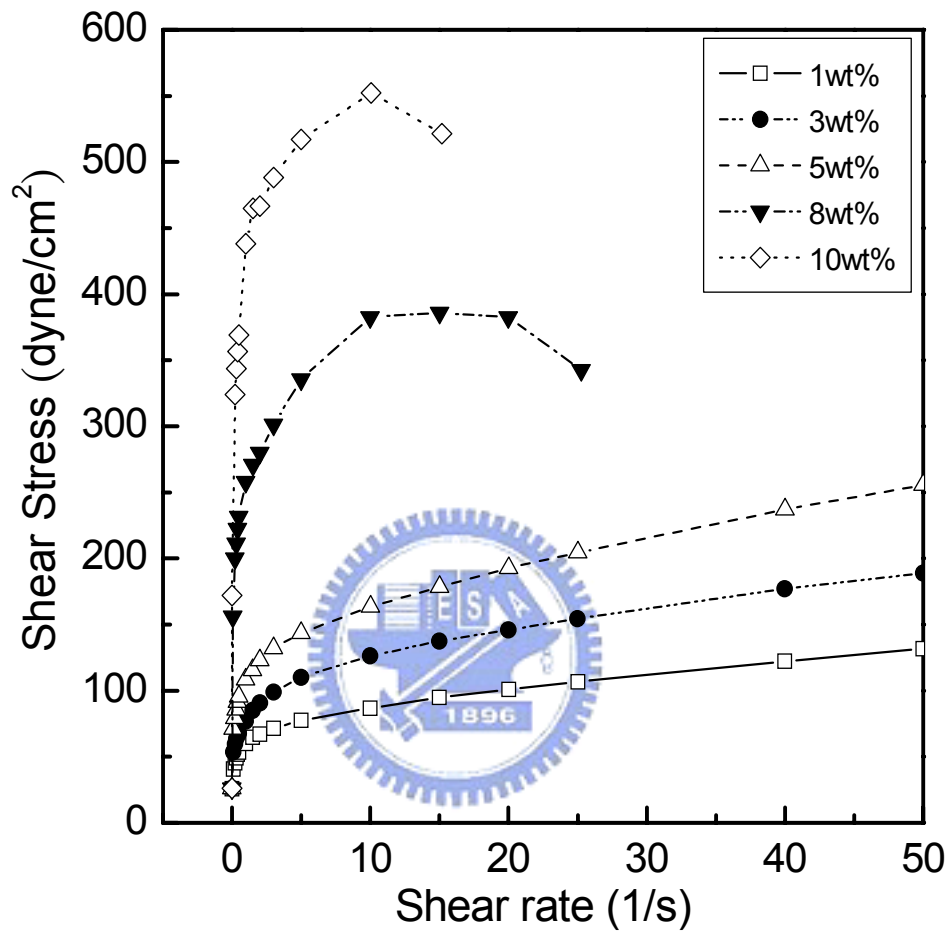


Figure 4-6(a). (a) Viscosity properties for simple flow models, (b) thixotropy properties of the pastes.

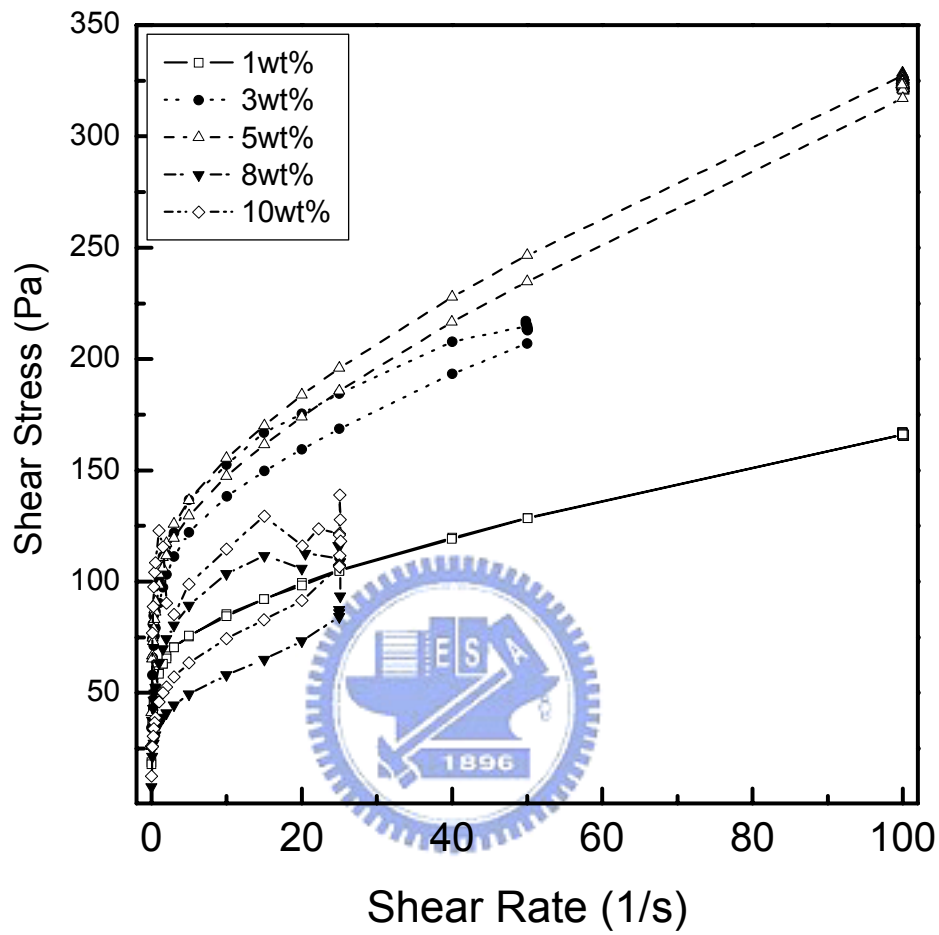


Figure 4-6(b). (a)Viscosity properties for simple flow models, (b) thixotropy properties of the pastes.

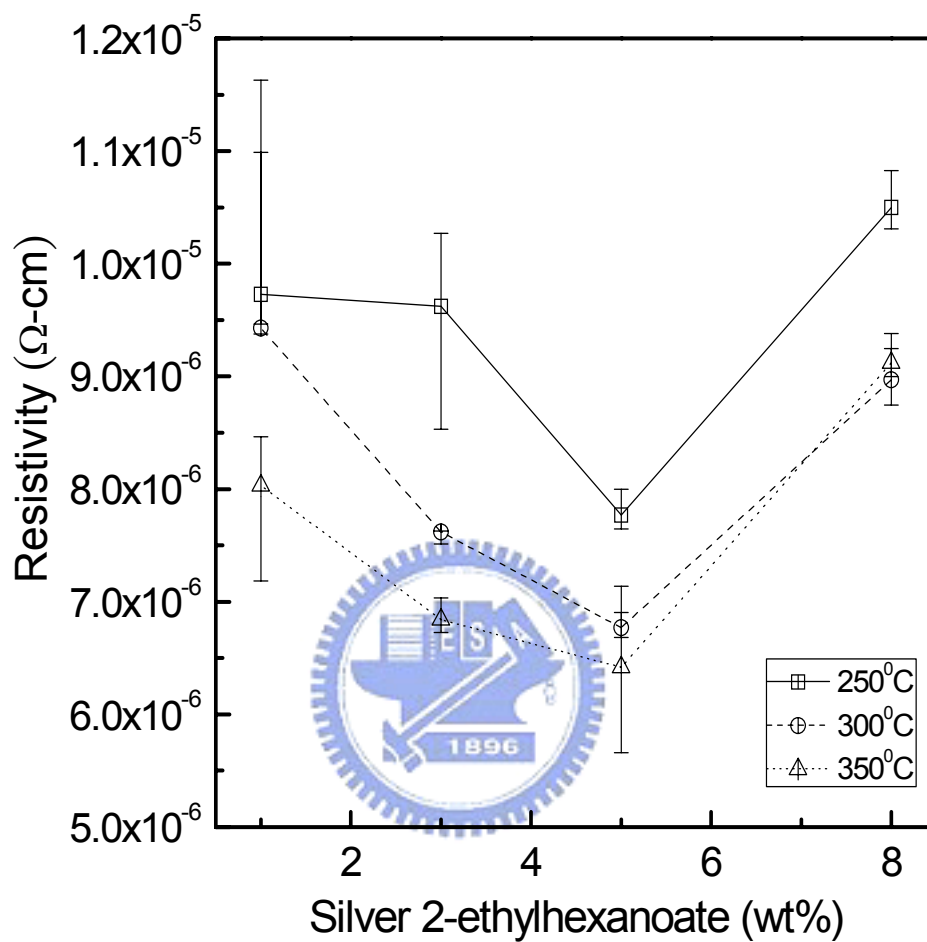


Figure 4-7. Resistivities of silver films with additions of various amounts of silver 2-ethylhexanoate and cured at different temperatures.

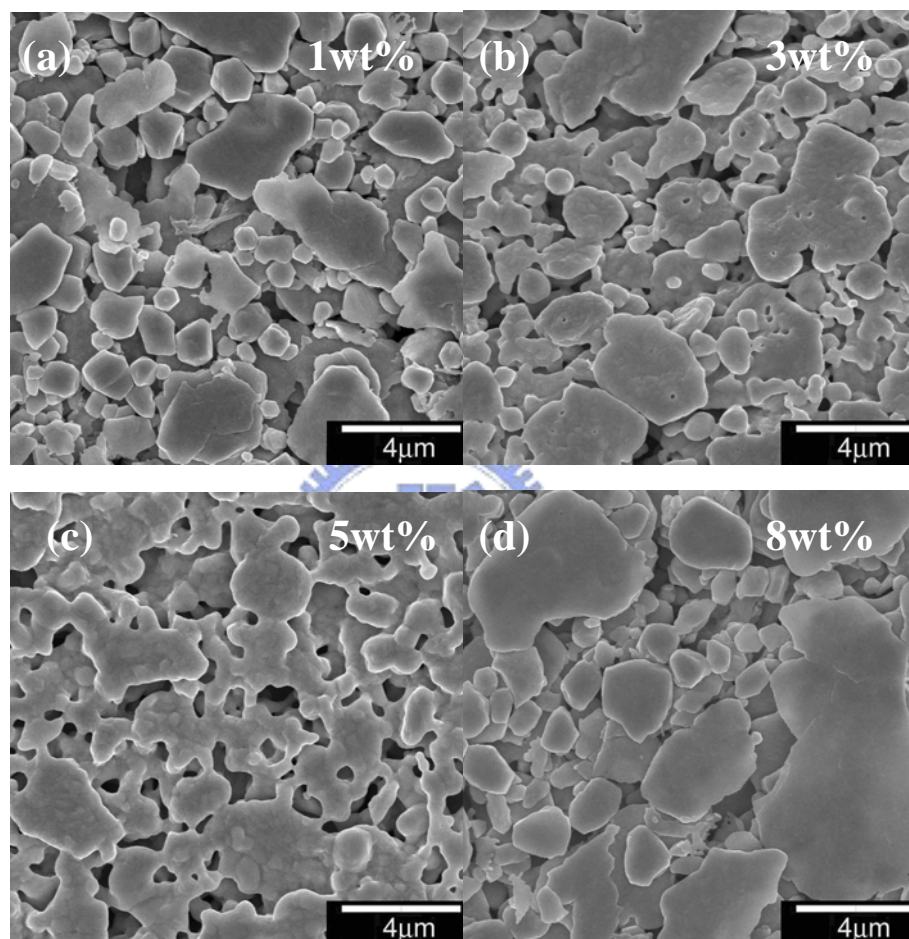


Figure 4-8. SEM micrographs of the silver films with additions of various amounts of 2-ethylhexanoate and cured at 250°C for 10min.

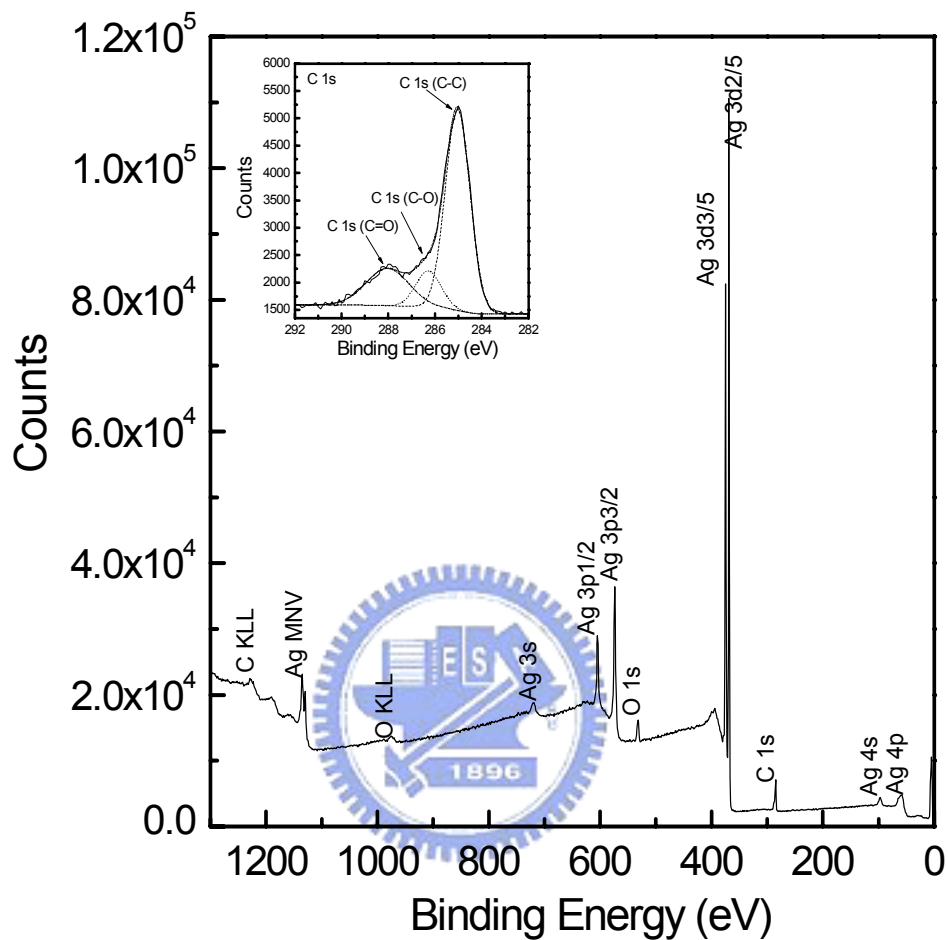


Figure 4-9(a). ESCA results of the silver films with additions of various amounts of 2-ethylhexanoate and cured at 250°C for 10min for wide binding energy. (b) for C-C binding.

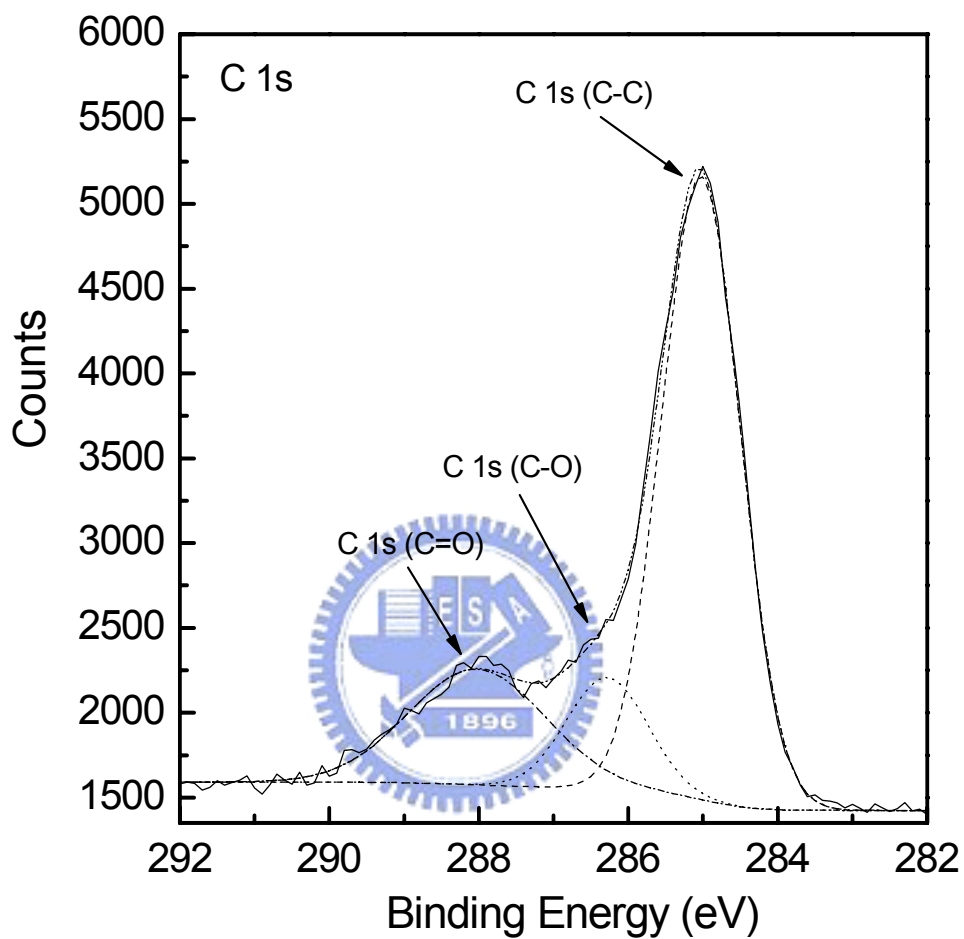


Figure 4-9(b). ESCA results of the silver films with additions of various amounts of 2-ethylhexanoate and cured at 250°C for 10min for wide binding energy. (b) for C-C binding.

Table 4-1. Mass fragments due to the thermal decomposition of silver 2-ethylhexanoate in air and He atmospheres.

| m/z | Fragment(s) | Peak in dry air at temperature (°C) | Peak in He at temperature (°C) |
|--------|------------------------------------|-------------------------------------|--------------------------------|
| TGA-MS | | | |
| 14 | CH ₃ | 50-350 ^{M*} | |
| 18 | H ₂ O | | 50-350 ^{S*} |
| 28 | CO | 50-350 ^{S*} | 50-350 ^{S*} |
| 32 | O ₂ | 50-350 ^{M*} | 50-350 ^{W*} |
| 42 | CH ₂ CO | | 180-350 ^{M*} |
| 44 | CO ₂ | 200-350 ^{M*} | 200-350 ^{M*} |
| 57 | C ₄ H ₉ | 180-350 ^{M*} | |
| 72 | C ₂ H ₅ COOH | 180-350 ^{M*} | 160-350 ^{S*} |
| 86 | C ₅ H ₁₀ O | 180-350 ^{M*} | 160-350 ^{S*} |
| 98 | C ₇ H ₁₄ | 180-320 ^{W*} | 180-350 ^{M*} |
| 115 | C ₇ H ₁₅ O | 185-320 ^{W*} | 160-350 ^{M*} |
| 127 | C ₈ H ₁₅ O | 220-250 ^{W*} | 240-320 ^{W*} |

*S=strong M=middle W=weak